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Thermolysis of Imidates – a New Method for the Generation of Carbonyl Ylides

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Thermolysis of dimethyl 2-[(3-oxo-3*H*-isoindol-1-yl)oxy]malonate (**8**) promotes a [1,4]-H shift in the imidic –N=C–O–CH– fragment of the starting molecule, which leads to a reactive carbonyl ylide. This carbonyl ylide can be trapped by the C=N bond of imidates and imines, as well as the C=O bond of benzaldehyde. The corresponding cycloadducts **11**, **14**, and **15** are formed regioselectively in good yields (60–95%) and with high stereoselectivity. In the case of **11**, the minor cycloadduct in solution undergoes an isomerization to give the more stable stereoisomer. The structures of two cycloadducts, *i.e.*, **11a** and **14a**, have been established by X-ray crystallography.

1. Introduction. – Carbonyl ylides are highly reactive intermediates of increasing interest, which are frequently applied for the purposes of organic chemistry [1][2], particularly in natural product synthesis [3]. Several methods [4-8] for the generation of these reactive species from different classes of compounds enable the introduction of a wide variety of functionalities into the structure of the final product. In combination with high efficiency and selectivity of the reactions, this often makes carbonyl ylides the key intermediates in the design of synthetic strategies [3]. The known scope and limitations, together with the evident usefulness of the chemistry of carbonyl ylides in organic synthesis, make further investigations in this area desirable. We would like to report here a recently discovered new method for the generation of carbonyl ylides.

The known methods for the generation of carbonyl ylides **1** involve photochemical and thermal ring opening of substituted oxiranes **2** [4], thermal decomposition of substituted 1,3,4-oxadiazolines **3** [5], 1,3-elimination reactions of trimethylsilyl substituted chloromethyl ethers **4** [6], SmI₂ mediated generation of nonstabilized carbonyl ylides (**1**; R³, R⁴ = R¹, R²) from α -iodomethyl trialkylsilyl ethers **5** [7], thermal decomposition of organomercury compounds **6** in the presence of carbonyl compounds [8], and decomposition of α -diazocarbonyl compounds **7**, mostly with Rh or Cu complexes, in the presence of compounds which contain a C=O group in their structure [3] (*Scheme 1*). The latter method greatly advanced the application of carbonyl ylides to the synthesis of complex natural products.

Scheme 1. Methods for the Generation of Carbonyl Ylides

An additional possibility for the generation of carbonyl ylides from imidates was observed accidentally. In connection with some recent work from our laboratory [9], we

investigated the possibility of a thermal isomerization of imidates into their *N*-alkyl derivatives [10] in the series of recently synthesized products. In particular, attempts were made to carry out this isomerization in the case of phthalimide *O*-alkylimidate **8**.

2. Results and Discussion. – The fused imidate **8** was synthesized by using Rh-catalyzed decomposition of dimethyl diazomalonate (**9**) in the presence of phthalimide (**10**) [9c] (*Scheme 2*).

Scheme 2. Synthesis of the Object of Investigation

The thermolysis of **8** was investigated at 115–125°, and the progress of the reaction was followed by using TLC. Complete transformation of the starting material was observed after 1 h at 120°. Heating of **8** above its melting point (113–115°) gives rise to the formation of a 3:1 mixture of two diastereoisomers as racemates. Their structures correspond with the pentacyclic 1,3-oxazolidines **11a** and **11b**, which are dimers of **8** (*Scheme 3*). The corresponding *N*-alkylated phthalimide, *i.e.*, dimethyl 2-(phthalimid-2-yl)malonate, could not be detected in the mixture.

Scheme 3. Thermal Dimerization of **8**

The structure of the major dimer **11a** was established unambiguously by an X-ray crystal-structure determination (*Fig. 1*), whereas that of the minor isomer **11b** was elucidated by comparison of the spectroscopic data of the two products.

Fig. 1. *ORTEP* plot [11] of one of the two conformations of the molecular structure of **11a**
(arbitrary numbering of the atoms; 50% probability ellipsoids)

Since the space group is centrosymmetric, the compound in the crystal is racemic. The asymmetric unit contains one molecule of **11a** plus one molecule of CH₂Cl₂. The ester moieties of the dimethyl 2-hydroxymalonate group are disordered over two conformations with the major one being present in approximately 60% of the molecules. The NH group forms weak bifurcated H-bonds. One is an intramolecular interaction with the MeO group of the nearest adjacent ester group in the molecule, *i.e.*, one of the ester MeO groups at the 1,3-oxazolidine ring. This interaction forms a seven-membered loop, which has a graph set motif [12] of S(7). The second interaction is an intermolecular H-bond with the ester C=O group of the second ester group at the 1,3-oxazolidine ring of an adjacent molecule. In turn, the latter molecule has an identical interaction with the first molecule, so that this interaction links pairs of centrosymmetrically related molecules to give dimers with a graph set motif of R²₂(14).

As a likely reaction mechanism for the formation of structure **11** as a mixture of diastereoisomers, we assume a thermal generation of an intermediate carbonyl ylide **1a** via a reversible [1,4]-H shift in **8** (*Scheme 4*). Subsequent 1,3-dipolar cycloaddition of **1a** to the C=N bond of another molecule of **8** leads to the compounds of type **11**.

Scheme 4. Proposed Mechanism for the Formation of the Dimers **11a** and **11b**

Two intriguing points have attracted our attention in this chemical process. The first is the generation of the carbonyl ylide **1a** upon thermolysis of the *O*-alkylimidate **8**¹). To the best of our knowledge (*cf.* [1-3]), the observed transformation is an unprecedented generation of a carbonyl ylide and, thus, is the first example of a [1,4]-H migration leading to a carbonyl ylide (*Scheme 4*)²). The crystal-structure of **8** [9c] shows that the molecule adopts a *s-cis*-conformation at the exocyclic C,O bond, which implies a favorable spatial arrangement for an interaction between the malonate H-atom and the lone electron pair of the N-atom of the C=N group. Taking into consideration the reasonably high acidity and mobility of the H-atom in the 1,3-dicarbonyl moiety of **8**, it might be expected that this H-atom can easily migrate to the N-atom of the C=N group, thereby converting the imidate **8** into the carbonyl ylide **1a**. The latter then reacts with a second molecule of **8** in a [2+3] cycloaddition to give the 1,3-oxazolidines **11**.

The second attractive aspect of the formation of **11** is the fact that this is actually the first example of intermolecular [1,3]-dipolar cycloadditions in the series of imidic carbonyl ylides. As was established previously, carbonyl ylides, which were generated from sulfonimides or imides and Rh(II)-ketocarbenoids, do not give cycloadducts, in contrast to reactions with intramolecular counterparts [9a].

¹) The formation of 1,3-dipoles *via* an H-shift, *i.e.*, the thermal generation of azomethine ylides from imines *via* 1,2-prototropy, has been extensively studied by *Grigg* and coworkers [13].

²) The stabilization of reactive 1,3-dipoles *via* [1,4]-H shifts is a well-known reaction (*e.g.*, in carbonyl ylides [14], in thiocarbonyl ylides [15], and in nitrile ylides [16]).

An interesting transformation was observed while NMR data for the minor isomer **11b** were collected. Due to its low solubility in CDCl_3 , ^{13}C -NMR spectra were measured in $(\text{D}_6)\text{DMSO}$. While doing so, **11b** isomerizes to give the more stable isomer **11a** within 5–7 h at room temperature (*Scheme 5*). Most likely, the reaction mechanism involves an intramolecular H-transfer in **11b** from the CONH group to the neighboring C=O group with simultaneous opening of the 1,3-oxazolidine ring, *i.e.*, a retro-ene type reaction. During this transformation to **12**, the former *spiro* C-atom loses its chirality. In the intermediate **12**, the isoindolinone fragments are able to rotate about the C–O bonds between them and can occupy an arrangement preferable for the ring closure to give the more stable isomer **11a**.

Scheme 5. Isomerization of **11b** into **11a**

In further studies, C=N bonds of imines were tested as possible dipolarophiles [17]. Heating a mixture of the imidate **8** and benzylidenemethylamine (benzaldimine, **13**) for 6 h at 120° resulted in the formation of a *ca.* 1:5 mixture of two racemic diastereoisomers of the spirocyclic 1,3-oxazolidines **14a** and **14b** in 70% yield (*Scheme 6*). The structures of the products were elucidated on the basis of their spectroscopic data and elemental analyses, and that of the minor product **14a** was unambiguously established by an X-ray crystal-structure determination (*Fig. 2*).

Scheme 6. Thermal reaction of **8** with benzaldimine (**13**)

Fig. 2. *ORTEP plot* [11] of the molecular structure of **14a** (arbitrary numbering of the atoms; 50% probability ellipsoids).

Since the space group is centrosymmetric, the compound in the crystal is racemic. The 1,3-oxazolidine ring has an envelope conformation puckered on the Ph-substituted C(12). The Ph substituent is in a *cis* relationship with the N-atom of the isoindoline moiety. The NH atom forms an intermolecular H-bond with one of the ester C=O groups of a neighboring molecule. The interaction links the molecules into extended chains which run parallel to the [010] direction and can be described by a graph set motif [12] of C(7).

Due to the inversion of the N-atom in the 1,3-oxazolidine ring, an equilibrium between two conformations is set up for each diastereoisomer. Signals of both conformers of **14a** and **14b** may be observed after 24 h at 23° in CDCl₃ solution (see experimental part).

An indirect confirmation for the proposed mechanism of the isomerization **11b** → **11a**, which involves a proton transfer onto the amidic C=O group (*Scheme 5*), is the observation that **14a** and **14b** are stable in (D₆)DMSO even after 10 d at room temperature, *i.e.*, no isomerization could be observed.

The cycloaddition of carbonyl ylide **1a** with the C=O bond of aldehydes was also tested. Heating a mixture of **8** and benzaldehyde (**15**) for *ca.* 5 h at 120° led to a *ca.* 71:1 mixture of the diastereoisomeric dioxolanes **16a** and **16b** in 72% yield (*Scheme 7*). The structures of **16a** and **16b** were established on the basis of their spectroscopic data and by comparison of these data with those obtained for the diastereoisomers **11a,b** and **14a,b**.

Scheme 7. Thermal Reaction of **8** with benzaldehyde (**15**)

3. Conclusion. – In the present paper we report on a new possibility for the generation of carbonyl ylides by thermal [1,4]-H shift in imidates. Subsequent intermolecular trapping of the generated carbonyl ylide with C=N bonds of imidates and imines, as well as the C=O bond of aldehydes, gives the corresponding cycloadducts with high yields and stereoselectively. The discovered transformation of imidates of type **8** is a method for the preparation of rare labile polyfunctional spirocyclic structures with three heteroatoms attached to the spiro-center. Molecules with such structural fragments are of great importance in the chemistry of natural products [17][18]. For this reason, detailed investigations of the discovered transformations are in progress.

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Experimental Part

1. *General.* M.p.: *Büchi B-540* apparatus, in capillaries; uncorrected. IR Spectra: *Perkin Elmer Spectrum One CSI Beam Splitter* spectrophotometer; in KBr. ^1H - and ^{13}C -NMR Spectra: *Bruker AV-300*, *Bruker ARX-300* and *Avance DRX-600* instruments; working frequencies 300 and 600 MHz for ^1H - and 75.45 and 150.92 MHz for ^{13}C -NMR spectra, resp.; in CDCl_3 or $(\text{D}_6)\text{DMSO}$, with Me_4Si ($=0$ ppm) as internal standard; J in Hz. MS: *Finnigan TSQ 700*, *Bruker Autoflex I MALDI-TOF* or *Bruker EsquireLC* spectrometers. Microanalyses were performed on a *Heraeus CHNS Rapid Analyzer*.

All reactions were carried out in carefully dried and distilled solvents. *N*-Benzylidenemethylamine (**13**) and benzaldehyde (**15**) are commercially available (*Fluka*) and were distilled before use. All reactions were monitored by thin-layer chromatography (TLC) on silica gel 60-F₂₅₄ sheets (*Merck*) using UV-light for visualization. Silica gel 60 (0.040–0.063 mm, *Merck*) was used for column chromatography (CC).

2. *Thermolysis of Dimethyl 2-[(3-Oxo-3H-isoindol-1-yl)oxy]malonate (8)* [9a].

Dimethyl (9b'RS,4'SR)-1',9b'-dihydro-9b'-[di(methoxycarbonyl)]methoxy-3,5'-dioxospiro[isoindole-1,4'-(1',3')oxazolo[4',3'-a]isoindole]-1',1'-dicarboxylate (11a) and *Dimethyl (9b'RS,4'RS)-1',9b'-dihydro-9b'-[di(methoxycarbonyl)]methoxy-3,5'-dioxospiro[isoindole-1,4'-(1',3')oxazolo[4',3'-a]isoindole]-1',1'-dicarboxylate (11b)*. The *O*-alkylimidate **8** (1.5 g, 5.4 mmol) was placed in a round bottom flask with a magnetic stirrer and slowly heated in an oil bath until the compound melted to give a colorless oil (temperature of the oil bath 120°). Stirring was continued at 120–125° as long as starting material was present in the mixture (*ca.* 1 h, TLC), and then the mixture was cooled to r.t. The obtained crystalline residue contains the isomers **11a** and **11b** as a chromatographically inseparable ~3:1 mixture. This mixture was passed through a plug of silica gel to remove polymeric by-products by using CH₂Cl₂/AcOEt (2:1) as solvent. Isomer **11a** could be crystallized from the main fraction using CH₂Cl₂/petroleum ether (1:1).

11a: Yield: 0.73 g (48%). Colorless crystals. M.p. 196–197° (CH₂Cl₂/petroleum ether); *R_f* = 0.44 (CH₂Cl₂/hexane, 3:1). IR (KBr): 3385*m*, 2959*m*, 1767*s*, 1755*s*, 1754*s*, 1748*s*, 1746*s*, 1729*s*, 1621*m*, 1549*s*, 1437*s*, 1402*s*, 1309*s*, 1267*s*, 1036*s*, 715*s*, 578*m*. ¹H-NMR (CDCl₃): 3.43, 3.45, 3.55, 4.05 (4*s*, 3H each, 4 MeO); 4.39 (*s*, CHO); 6.81 (*s*, NH); 7.44–7.90 (*m*, 8 arom. H). ¹H-NMR ((D₆)DMSO): 3.44, 3.47, 3.54, 4.00 (4*s*, 3H each, 4 MeO); 4.43 (*s*, CHO); 7.63–7.99 (*m*, 8 arom. H); 8.96 (*s*, NH). ¹³C-NMR (CDCl₃): 52.6, 52.8, 53.4, 53.7 (4 MeO);

72.2 (CHO); 87.3 (C(1)); 101.2 (C(9b)); 102.9 (C-spiro); 123.3, 123.5, 124.8, 125.6, 130.1, 130.8, 132.1, 133.08, 133.14, 134.2, 136.1, 143.3 (arom. C); 163.3, 165.1 (2 MeO₂C); 165.6 (C(5)); 165.7, 166.7 (2 MeO₂C); 167.6 (CONH). ¹³C-NMR ((D₆)DMSO): 52.7, 53.0, 53.3, 53.7 (4 MeO); 72.1 (CHO); 87.1 (C(1)); 100.6 (C(9b)); 102.3 (C-spiro); 122.6, 123.3, 124.2, 125.6, 129.9, 131.1, 132.1, 133.10, 133.15, 133.3, 133.7, 143.5 (arom. C); 163.1, 164.6 (2 MeO₂C); 164.9 (C(5)); 165.1, 165.6 (2 MeO₂C); 167.7 (CONH). EI-MS (70 eV): 554 (4, *M*⁺), 523 (26), 495 (50), 407 (9), 289 (10), 277 (100), 262 (8), 230 (6), 147 (7), 130 (62), 84 (21), 49 (22). Anal. calc. for C₂₆H₂₂N₂O₁₂ (554.46): C 56.31, H 4.00, N 5.05; found: C 56.29, H 3.95, N 4.94.

11b: Yield: 12% (based on ¹H-NMR data). The following NMR data were taken from ¹H- and ¹³C-NMR spectra of a mixture of **11a** and **11b**. ¹H-NMR ((D₆)DMSO): 3.52, 3.56, 3.71, 3.73 (4s, 3H each, 4 MeO); 4.32 (s, CHO); 7.63–7.99 (m, 8 arom. H); 9.30 (s, NH). ¹³C-NMR ((D₆)DMSO): 52.6, 52.9, 53.3, 53.5 (4 MeO); 71.2 (CHO); 89.3 (C(1)); 93.1 (C(9b)); 98.5 (C-spiro); 119.2, 121.9, 122.7, 126.2, 131.4, 132.2, 132.6, 133.6, 133.9, 134.0, 138.9, 141.5 (arom. C); 161.9, 162.0, 165.0, 165.5, 165.6, 167.9 (5 C=O).

3. Reaction of **8** with N-Benzylidenemethylamine (**13**). Dimethyl (2'SR,4'SR)-2,3-Dihydro-3'-methyl-3-oxo-4'-phenylspiro[isoindole-1,2'-[1',3']oxazolidine]-5',5'-dicarboxylate (**14a**) and Dimethyl (2'RS,4'SR)-2,3-Dihydro-3'-methyl-3-oxo-4'-phenylspiro[isoindole-1,2'-[1',3']oxazolidine]-5',5'-dicarboxylate (**14b**). A stirred mixture of **8** (0.3 g, 1.08 mmol) and **13** (1.2 g, 10.8 mmol) in a round bottom flask was heated to 120–125° until no **8** was present in the mixture (ca. 6 h, TLC). Then, the mixture was cooled to r.t. Excess imine **13** was evaporated *in vacuo*, and the isomers **14a** and **14b** were separated by CC (SiO₂, CH₂Cl₂/AcOEt 20:1).

14a: Yield: 0.043 g (11%). Colorless crystals. M.p. 195° (CH₂Cl₂/hexane). R_f = 0.6 (CH₂Cl₂/AcOOEt, 20:1). IR (KBr): 3360_s, 2953_w, 2851_w, 1744_s, 1734_s, 1724_s, 1625_w, 1473_m, 1391_m, 1308_s, 1236_s, 1112_s, 973_m, 756_s, 704_m. ¹H-NMR (CDCl₃): 2.02 (s, MeN); 3.28, 3.80 (2s, 3H each, 2 MeO); 5.19 (s, PhCH); 6.75 (s, NH); 7.33–7.84 (m, 9 arom. H). ¹³C-NMR (CDCl₃): 32.3 (MeN); 52.4, 53.2 (2 MeO); 76.9 (C(4')); 86.2 (C(5')); 106.5 (C-spiro); 122.6, 123.8, 128.4 (4C), 128.8, 130.3, 131.6, 132.3, 133.9, 142.8 (arom. C); 166.9, 167.3, 167.5 (3 C=O). ESI-MS (ESI): 419 (90, [M+Na]⁺), 397 (15, [M+H]⁺). Anal. calc. for C₂₁H₂₀N₂O₆ (396.39): C 63.63, H 5.09, N 7.07; found: C 63.12, H 5.10, N 6.99.

Selected ¹H-NMR signals of the second conformer: 2.05 (s, MeN); 3.29, 3.82 (2s, 3H each, 2 MeO); 5.21 (s, PhCH); 6.77 (s, NH).

14b: Yield: 0.23 g (59%). Colorless crystals. M.p. 210° (CH₂Cl₂/hexane). R_f = 0.4 (CH₂Cl₂/AcOEt, 20:1). IR (KBr): 3432_m, 3206_m, 2953_m, 2852_w, 1765_s, 1747_s, 1710_s, 1613_w, 1435_m, 1303_s, 1234_s, 1106_s, 1027_s, 972_w, 755_m, 704_m. ¹H-NMR (CDCl₃): 2.06 (s, MeN); 3.22, 3.83 (2s, 3H each, 2 MeO); 4.93 (s, PhCH); 6.62 (s, NH); 7.26–8.12 (m, 9 arom. H). ¹³C-NMR (CDCl₃): 31.4 (MeN); 52.2, 53.3 (2 MeO); 70.2 (C(4')); 87.6 (C(5')); 107.0 (C-spiro); 122.8, 124.5, 128.4 (4C), 128.7, 130.8, 131.9, 133.1, 134.5, 142.9 (arom. C); 166.8, 167.8, 169.1 (3 C=O). CI-MS: 397 (100, [M+H]⁺), 161 (30). Anal. calc. for C₂₁H₂₀N₂O₆ (396.39): C 63.63, H 5.09, N 7.07; found: C 63.32, H 5.11, N 6.98.

Selected ¹H-NMR signals of the second conformer: 2.07 (s, MeN); 3.23, 3.84 (2s, 3H each, 2 MeO); 4.94 (s, PhCH); 6.63 (s, NH).

4. Reaction of **8** with Benzaldehyde (**15**). Dimethyl (2'RS,4'SR)-2,3-Dihydro-3-oxo-5'-phenylspiro[isindole-1,2'-[1',3']dioxolan]-4',4'-dicarboxylate (**16a**) and Dimethyl (2'RS,4'RS)-2,3-Dihydro-3-oxo-5'-phenylspiro[isindole-1,2'-[1',3']dioxolan]-4',4'-dicarboxylate (**16b**). A stirred mixture of **8** (0.5 g, 1.8 mmol) and **15** (1.91 g, 18.0 mmol) in a

round bottom flask was heated to 120–125° until no **8** was present in the mixture (*ca.* 5 h, TLC). Then, the mixture was cooled to r.t. The excess of **15** was evaporated *in vacuo*, and the obtained isomers **16a** and **16b** were separated by CC (SiO₂, CH₂Cl₂/AcOEt 8:1 as eluent).

Major diastereoisomer: Yield: 0.49 g (71%). Colorless crystals. M.p. 184–185° (CH₂Cl₂/hexane). R_f = 0.5 (CH₂Cl₂/AcOEt, 8:1). IR (KBr): 3223 m , 3116 m , 2955 m , 1771 s , 1751 s , 1727 s , 1615 w , 1435 s , 1297 s , 1235 s , 1123 s , 1071 s , 1022 s , 834 m , 750 s , 700 m , 592 m . ¹H-NMR (CDCl₃): 3.16, 3.82 (2 s , 3H each, 2 MeO); 6.01 (s , CHO); 7.03 (s , NH); 7.31–8.14 (m , 9 arom. H). ¹³C-NMR (CDCl₃): 51.6, 52.6 (2 MeO); 81.5 (C(5')); 86.3 (C(4')); 113.9 (C-spiro); 122.2, 123.4, 125.5 (2C), 127.3 (2C), 128.1, 130.3, 130.5, 132.0, 132.3, 140.1 (arom. C); 165.4, 166.1, 167.7 (3 C=O). EI-MS: 384 (9, [M+H]⁺), 383 (9, M⁺), 277 (45), 237 (26), 236 (17), 162 (100), 149 (25), 148 (67), 130 (31), 121 (35), 107 (25), 105 (36), 103 (30), 90 (17), 77 (17), 76 (19), 59 (13). Anal. calc. for C₂₀H₁₇NO₇ (383.35): C 62.66, H 4.47, N 3.65; found: C 62.28, H 4.35, N 3.62.

Minor diastereoisomer: Yield: 0.07 g (1%). Colourless crystals. M.p. 144° (CH₂Cl₂/AcOEt). R_f = 0.7 (CH₂Cl₂/AcOEt, 8:1). IR (KBr): 3225 m , 3118 m , 2957 w , 1768 s , 1748 s , 1723 s , 1438 m , 1299 s , 1126 s , 1068 s , 1026 s , 755 s . ¹H NMR (CDCl₃): 3.18, 3.81 (2 s , 3H each, 2 MeO); 6.06 (s , CHO); 7.30 (s , NH); 7.30–7.53 (m , 9 arom. H). ¹³C-NMR (CDCl₃): 53.4, 54.1 (2 MeO); 83.9 (C(5')); 87.3 (C(4')); 115.7 (C-spiro); 122.2, 124.0, 126.8 (2C), 128.9 (2C), 129.7, 131.4, 131.5, 133.2, 133.7, 143.6 (arom. C); 166.4, 167.7, 167.9 (3 C=O). EI-MS: 384 (4, [M+H]⁺), 383 (5, M⁺), 162 (100), 148 (65), 105 (38).

5. X-Ray Crystal-Structure Determination of **11a** and **14a** (Table and Figs. 1 and 2)³).

³) CCDC–602890 and 664632 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre* via www.ccdc.cam.ac.uk/data_request/cif.

All measurements were performed on a *Nonius KappaCCD* area-detector diffractometer [20] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in *Table*, and views of the molecules are shown in *Figs. 1* and *2*. Data reduction was performed with *HKL Denzo* and *Scalepack* [21]. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Equivalent reflections were merged. The structures were solved by direct methods using *SIR92* [22], which revealed the positions of all non-H-atoms. The asymmetric unit of **11a** contains one molecule of **11a** plus one molecule of CH_2Cl_2 . The ester moieties of the methoxydiester group are disordered. Two positions were defined for each disordered atom of this substituent and refinement of the site occupation factors led to a value of 0.597(5) for the major conformation. Bond length and similarity restraints were applied to all chemically equivalent bond lengths and angles involving the disordered atoms, while corresponding atoms from the disordered conformations were restrained to have similar atomic displacement parameters. The non-H-atoms were refined anisotropically. The NH H-atoms of **11a** and **14a** were placed in the positions indicated by difference electron density maps and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms in the structures were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied. In **11a** and **14a**, five reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinements. Neutral atom scattering factors for non-H-atoms were taken from ref. [23], and the scattering

factors for H-atoms were taken from ref. [24]. Anomalous dispersion effects were included in F_c ; [25] the values for f' and f'' were those of ref. [26]. The values of the mass attenuation coefficients are those of [27]. All calculations were performed using the SHELXL97 [28] program.

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Table. Crystallographic Data for Compounds **11a** and **14a**

	11a	14a
Crystallized from	CH ₂ Cl ₂ /hexane	CH ₂ Cl ₂ /hexane
Empirical formula	C ₂₇ H ₂₄ Cl ₂ N ₂ O ₁₂	C ₂₁ H ₂₀ N ₂ O ₆
Formula weight	639.39	396.40
Crystal color, habit	colorless, prism	colorless, prism
Crystal dimensions [mm]	0.18 × 0.32 × 0.32	0.12 × 0.71 × 0.25
Temperature [K]	160(1)	160(1)
Crystal system	triclinic	monoclinic
Space group	<i>P</i> [−] ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2	4
Reflections for cell determination	8132	6184
2θ range for cell determination [°]	4–60	4–60
Unit cell parameters		
<i>a</i> [Å]	11.5975(3)	9.7406(2)
<i>b</i> [Å]	12.1163(4)	7.6247(2)
<i>c</i> [Å]	12.3839(4)	26.8311(6)
α [°]	61.733(1)	90
β [°]	81.268(2)	95.567(1)
γ [°]	67.182(2)	90
<i>V</i> [Å ³]	1411.62(8)	1983.32(8)
<i>D_x</i> [g cm ^{−3}]	1.504	1.327
μ(MoKα) [mm ^{−1}]	0.299	0.0983
Scan type	φ and ω	φ and ω
2θ _(max) [°]	60	60
Total reflections measured	35800	46475
Symmetry independent reflections	8251	5788
Reflections with <i>I</i> > 2σ(<i>I</i>)	5726	3242
Reflections used in refinement	8246	5783
Parameters refined; restraints	472; 59	270; 0
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2σ(<i>I</i>) reflections]	0.0567	0.0546
<i>wR</i> (<i>F</i> ²) (all data)	0.1571	0.1437
Weighting parameters [<i>a</i> ; <i>b</i>] ^a)	0.0678; 0.6110	0.0609; 0
Goodness of fit	1.041	1.024
Secondary extinction coefficient	0.010(3)	0.043(3)
Final Δ _{max} /σ	0.001	0.002
Δρ (max; min) [e Å ^{−3}]	0.54; −0.84	0.26; −0.25

a) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$

Legends

Scheme 1. Methods for the Generation of Carbonyl Ylides

Scheme 2. Synthesis of the Object of Investigation

Scheme 3. Thermal Dimerization of **8**

Scheme 4. Proposed Mechanism for the Formation of the Dimers **11a** and **11b**

Scheme 5. Isomerization of **11b** into **11a**

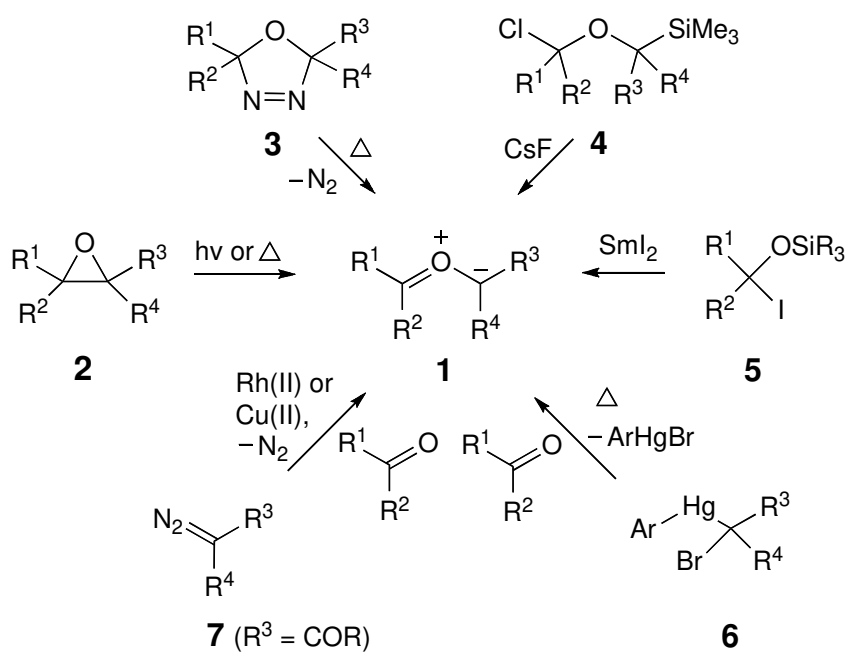
Scheme 6. Thermal reaction of **8** with benzaldimine (**13**)

Scheme 7. Thermal Reaction of **8** with benzaldehyde (**15**)

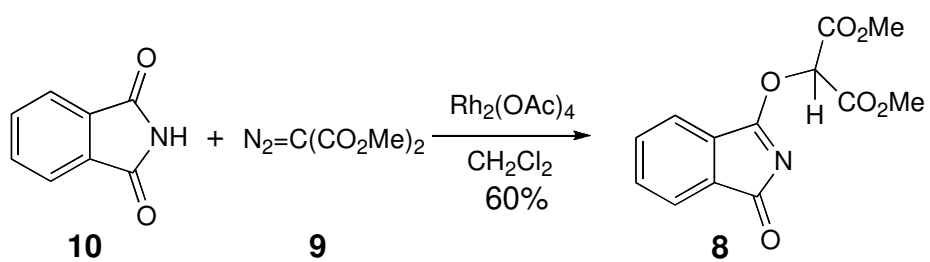
Fig. 1. *ORTEP* plot [11] of one of the two conformations of the molecular structure of **11a**
(arbitrary numbering of the atoms; 50% probability ellipsoids)

Fig. 2. *ORTEP* plot [11] of the molecular structure of **6a** (arbitrary numbering of the atoms;
50% probability ellipsoids).

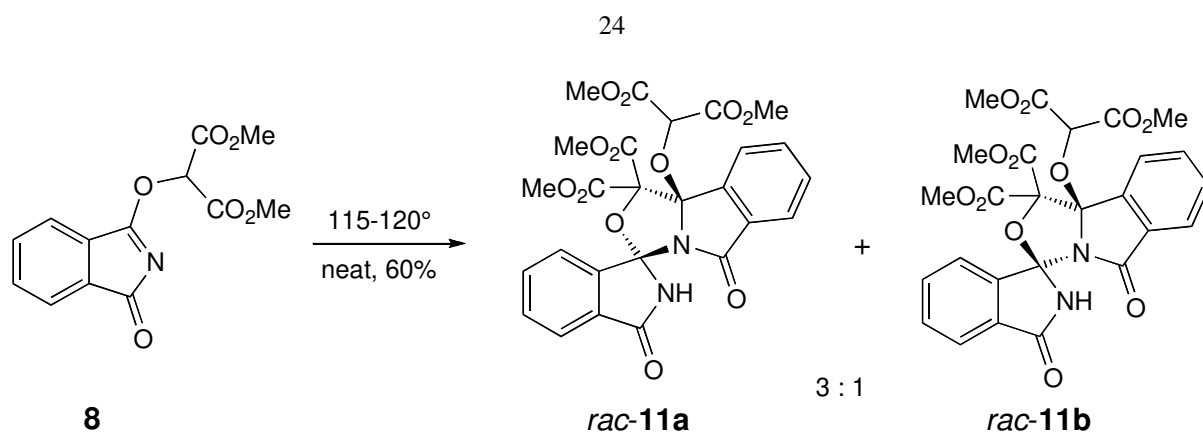
Scheme 1



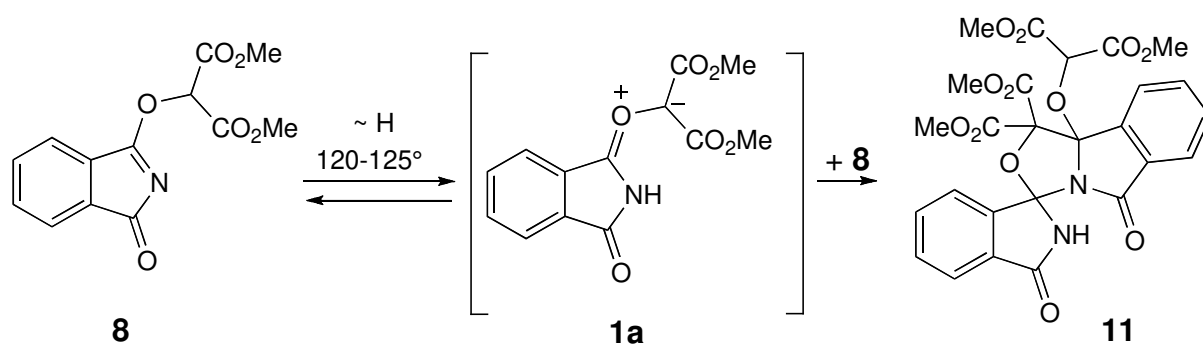
Scheme 2



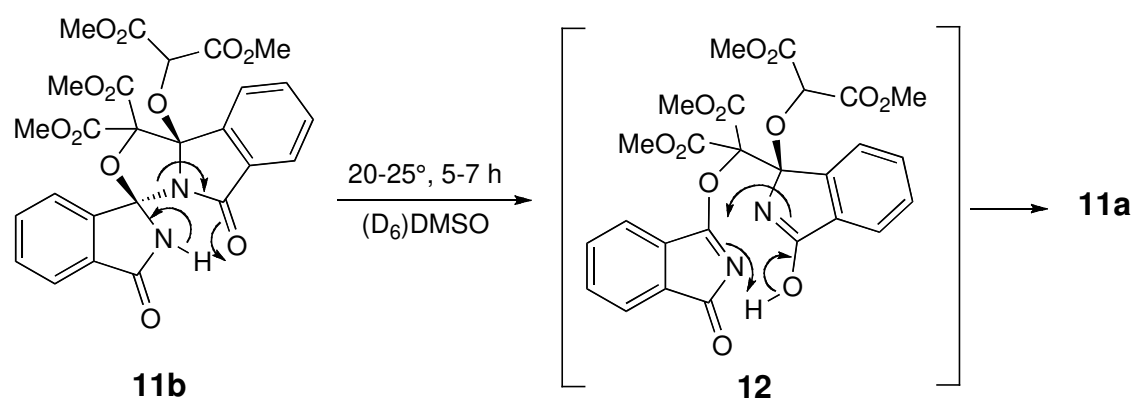
Scheme 3



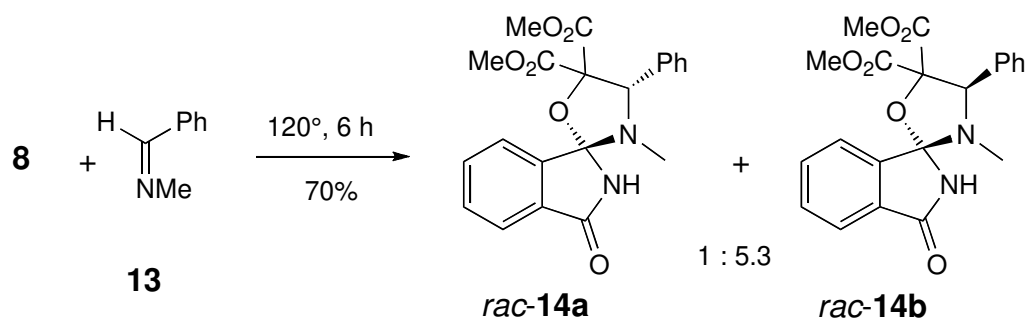
Scheme 4



Scheme 5



Scheme 6



Scheme 7

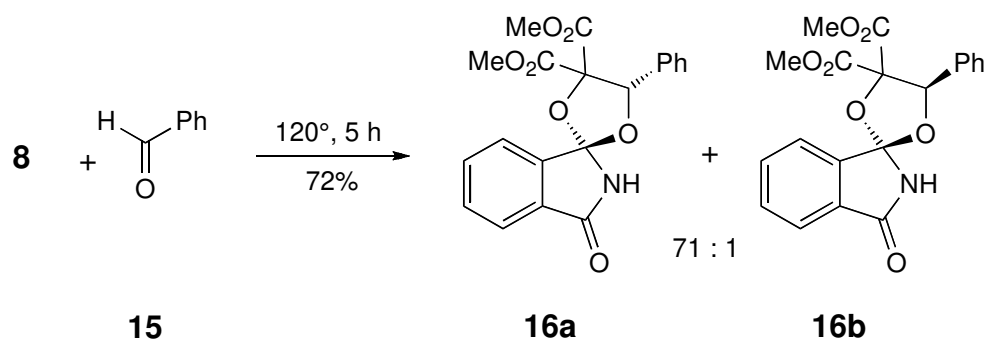


Figure 1

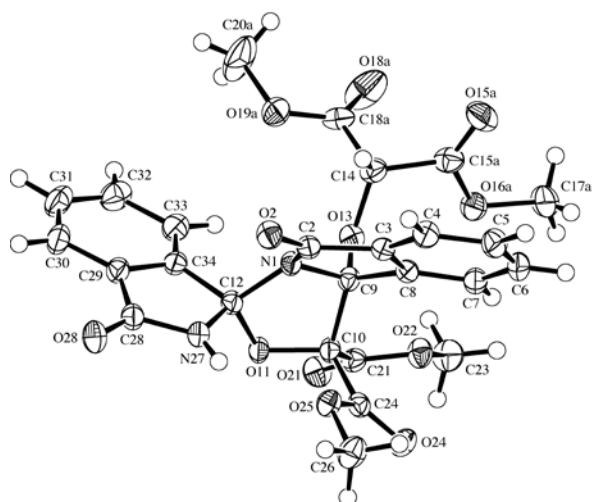
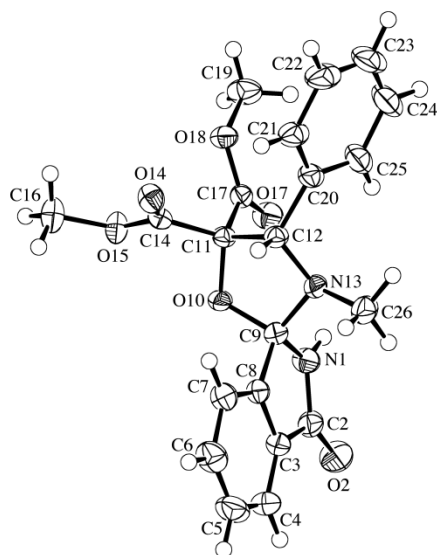


Figure 2



Graphical Abstract